



Publication number:

0 416 774 A1

-1- \* -

EUROPEAN PATENT APPLICATION

(21) Application number: 90309106.4

(51) Int. Cl.<sup>5</sup>: H01L 21/321

(22) Date of filing: 20.08.90

*etch*  
*H<sub>2</sub>O* → *H<sub>2</sub> + O<sub>2</sub>*  
*plasma*

The title of the invention has been amended  
(Guidelines for Examination in the EPO, A-III,  
7.3).

(30) Priority: 28.08.89 JP 218523/89  
02.11.89 JP 284711/89  
09.05.90 JP 117596/90

(43) Date of publication of application:  
13.03.91 Bulletin 91/11

*3-13-91*

(84) Designated Contracting States:  
DE FR GB

(71) Applicant: HITACHI, LTD.  
6, Kanda Surugadai 4-chome  
Chiyoda-ku, Tokyo 100(JP)

(72) Inventor: Fukuyama, Ryooji  
236-14, Nishitoyoi  
Kudamatsu-Shi, Yamaguchi-Ken(JP)  
Inventor: Kakehi, Yutaka  
7-13-11, Nijigaoka  
Hikari-Shi, Yamaguchi-Ken(JP)

Inventor: Nawata, Makoto  
1598-35 Nishitoyoi  
Kudamatsu-Shi, Yamaguchi-Ken(JP)  
Inventor: Kawahara, Hironobu  
68-31, Wakamiya, Kochi  
Kudamatsu-Shi, Yamaguchi-Ken(JP)  
Inventor: Sato Yoshiaki  
1611-10, Nishitoyoi  
Kudamatsu-Shi, Yamaguchi-Ken(JP)  
Inventor: Torii, Yoshimi  
1-3-17, Wakaba-cho  
Tachikawa-Shi, Tokyo(JP)  
Inventor: Kawayara, Akira  
1507-2, Higashitoyoi  
Kudamatsu-Shi, Yamaguchi-Ken(JP)  
Inventor: Sato, Yoshie  
1611-10, Nishitoyoi  
Kudamatsu-Shi, Yamaguchi-Ken(JP)

(74) Representative: Paget, Hugh Charles Edward  
et al  
MEWBURN ELLIS 2 Cursitor Street  
London EC4A 1BQ(GB)

(54) A method of etching a sample of aluminium-containing material.

(57) A post-etch treatment method is provided which is capable of imparting high corrosion prevention performance to aluminum-containing wiring films. The sample of aluminum-containing wiring material that is etched using the halogen-type gas is treated with the plasma of a gas that has an oxygen component, and the resist formed on the aluminum-containing wiring material is reacted with oxygen and is removed. Further, a plasma is generated using a gas having a hydrogen component or this gas is liquefied into droplets thereof on the sample surface, so that halogen components (Cl, Br, etc.) adhered to the aluminum-containing wiring material through the etching treatment are reacted with hydrogen and are effectively removed in the form of hydrogen chloride (HCl) or hydrogen bromide (HBr).

*etch Al<sub>2</sub> in Cl<sub>2</sub>*  
↓  
*ash resist in O<sub>2</sub>*  
↓  
*plasma post treat*  
*sample with H<sub>2</sub> plasma*  
*to remove corrosive Cl<sub>2</sub>*  
*residues*

EP 0 416 774 A1

## METHOD OF TREATING SAMPLES

BACKGROUND OF THE INVENTIONField of the Invention

The present invention relates to a method of treating samples, and particularly to a method of treating samples adapted to corrosion prevention treatment of aluminum-containing wiring materials after they have been subjected to the etching treatment.

Description of the Prior Art

According to a conventional method of treating aluminum-containing wiring materials as disclosed in, for example, Japanese Patent Publication No.41766/1983, a semiconductor wafer on which an aluminum-copper alloy film is formed is set in a reactive sputter-etching apparatus, the aluminum-copper alloy film is patterned using a plasma of such a gas as  $\text{BCl}_3$ ,  $\text{CCl}_4$ ,  $\text{PCl}_3$ ,  $\text{BBr}_3$  or the like, a hydrogen plasma is generated in the same apparatus, and the patterned aluminum-copper alloy film is exposed to the hydrogen plasma so as to be anti-corrosion treated.

In the above conventional technology, however, no attention has been given to removing residual or adhered matter after the etching treatment. In carrying out the etching treatment, in general, the aluminum-containing wiring material (hereinafter referred to as "wiring film") is masked with a photoresist or the like. The wiring film, in this case, may be aluminum-containing films ( $\text{Al}$ ,  $\text{Al-Si}$ ,  $\text{Al-Cu}$ ,  $\text{Al-Si-Cu}$ , etc.) and laminated wiring films such as aluminum-containing film + barrier metal, cap metal, reflection-preventing film + aluminum-containing film + barrier metal. (The barrier metal is composed of  $\text{TiW}$ ,  $\text{TiN}$  or the like, and is provided between the silicon substrate and the aluminum-containing film, in order to prevent defective junction due to mutual diffusion of the silicon substrate and the aluminum-containing film and to prevent the wiring resistance from increasing due to the precipitation of silicon in the aluminum-containing film. The cap metal is composed of  $\text{TiW}$ ,  $\text{TiN}$ ,  $\text{MoSi}$ , or the like, and is used as the uppermost layer of the wiring film of a laminated structure, or is used as the reflection-preventing film. The reflection-preventing film is formed on the aluminum film to suppress the reflection of light at the time of exposure, so that there is formed a resist pattern faithful to the mask.) The etching treatment is effected to treat the wafer on which the wiring

film is formed using the plasma of a single gas of the type of halogen such as  $\text{BCl}_3$ ,  $\text{Cl}_2$ ,  $\text{CCl}_4$ ,  $\text{SiCl}_4$ ,  $\text{HBr}$ ,  $\text{BBr}_3$  or the like, or a mixture gas thereof. The etching treatment is usually the one that is called reactive ion etching. With the reactive ion etching, the wiring film is etched maintaining a pattern faithful to the mask due to the interaction of radicals and ions in the plasma of the halogen-type gas, and the wiring pattern is obtained.

On the thus etched wiring pattern remains a photoresist (hereinafter referred to as "resist") which is a masking material. Halogen components in the plasma adhere on the surface of the resist during the etching and halogen components are implanted due to the bombardment of ions. On the side wall of the etched wiring pattern are adhered the halogen components during the etching or the resist components sputtered by the bombardment of ions. Moreover, aluminum component of the once etched wiring film adhere on the side walls again thereby to form a layer that is called side wall. This layer consists of such components as aluminum, chlorine, carbon, hydrogen, etc. that are adhered in a random fashion.

According to the above-mentioned conventional technology, a hydrogen plasma is generated in the apparatus after the etching treatment, and the patterned aluminum-copper film is exposed to the hydrogen plasma so that the aluminum-copper alloy film is anticorrosion-treated. In the treatment with hydrogen plasma, the halogen components adhered to the surfaces between the resist and the wiring pattern or adhered to the portions very close to these surfaces, undergo the reaction with hydrogen in the hydrogen plasma and can be removed as hydrogen chloride ( $\text{HCl}$ ) or hydrogen bromide ( $\text{HBr}$ ). However, the halogen components remaining in the resist and in the side walls are not allowed to come in contact with the hydrogen plasma and cannot be removed. Therefore, corrosion easily takes place in the wiring film due to the local battery action between the wiring film materials (between different metals) of the laminated structure or due to halogen components in the side wall (hereinafter referred to as "residual adhered matter").

Japanese Patent Laid-Open No.43132/1987 can be cited as a prior art related to the present invention. This prior art discloses a method of plasma treatment to remove organic film (resist) on the silicon substrate in the plasma of an oxygen gas obtained by adding a compound containing at least carbon or oxygen to the oxygen, e.g., by adding methanol ( $\text{CH}_3\text{OH}$ ) to the oxygen. According to this prior art, the rate of removing resist is

as shown in Fig. 2. It is, however, also allowable to directly treat the sample 16 with the plasma generated in the plasma generating chamber 17 without employing the porous plate. Further, the plasma is generated using microwaves. It is, however, also allowable to employ an RIE apparatus of the type of parallel flat plates using high-frequency electric power or any other system using high-frequency electric power such as a cylindrical-type apparatus, provided it is capable of generating plasma that contains hydrogen component and oxygen component.

In this embodiment, furthermore, the etching treatment and the post-etch treatment are incorporated in the same apparatus as shown in Fig. 1 and are continuously carried out. The invention, however, is in no way limited thereto only. That is, when the resist and the residual adhered matter are to be removed simultaneously, the subsequent additional treatment with the plasma of oxygen may be carried out in a separate treatment chamber which is provided on the outside of the apparatus that is shown in Fig. 1.

Furthermore, the resist may be removed by the widely known ashing treatment using the plasma of a mixture gas consisting of oxygen gas and a fluorine-type gas. The ashing treatment with the plasma of a mixture gas of oxygen gas and fluorine-type gas is effective for the corrosion prevention treatment particularly when a silicon-type material is contained in the resist material for forming pattern. When the silicon-type material (silicon-type inorganic resist or silicon photoresist) is used as the resist material, the ashing treatment with the oxygen radicals permit the silicon in the resist material to react with oxygen radicals to form silicon oxide that stays thereon, making it difficult to sufficiently carry out the ashing treatment for the resist. The remaining resist causes the wiring to corrode due to the residual chlorine or stays as foreign matter when an insulating film is to be formed on the wiring film causing poor insulation of the circuit, and deteriorates the yields of production. Therefore, the resist should be removed as much as possible.

The ashing treatment with the plasma of mixture gas of oxygen gas and fluorine-type gas is carried out after the plasma treatment (corrosion prevention treatment) that uses methanol or the mixture gas of methanol and oxygen, and that is effected after the etching treatment. Therefore, when the silicon-type material is used as the resist material component, the residual adhered matter and the resist that stay on the wiring film after the etching treatment can be effectively removed to accomplish high corrosion prevention performance. In the ashing treatment using the plasma of a mixture gas of oxygen and fluorine-type gas, fur-

procedure of treatment using the apparatus of Fig. 1;

Fig. 4 is a diagram showing residual quantity of chlorine which shows the effect of corrosion prevention treatment according to the present invention;

Fig. 7 is a vertical section view illustrating a sample treatment apparatus with which a second embodiment of the present invention is put into practice;

Fig. 8 is a diagram showing a curve of saturated vapor pressure;

Fig. 9 is a vertical section view illustrating a sample treatment apparatus with which a third embodiment of the present invention is put into practice in relation to the second embodiment; and

Fig. 10 is a vertical section view of a load lock chamber illustrating a fourth embodiment of the present invention in relation to the second embodiment.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[Examples]

An embodiment of the present invention will be described in conjunction with Figs. 1 to 6.

Fig. 1 shows a continuously treating apparatus which is capable of continuously carrying out the etching treatment and the post-etch treatment under vacuum condition. A buffer chamber 3 defines space from load lock chambers 4, 9 through an etching chamber 6 up to a post-etch treatment chamber 8. Here, each of the buffer chamber 3, load lock chambers 4, 9, etching chamber 6, and post-etch treatment chamber 8 can be independently partitioned by air-tight means and can be evacuated by an exhaust device (not shown). A load-side cassette 1 is disposed to be opposed to the load lock chamber 4, and a go-straight arm 2 is arranged therebetween. An unload-side cassette 11 is disposed to be opposed to the load lock chamber 9, and a go-straight arm 10 is arranged therebetween.

In this apparatus, the process flows as described below. First, a sample (wafer in this case) that is to be treated is introduced into the load lock chamber 4 which is open to the atmosphere from the load-side cassette 1 by the go-straight arm 2. Thereafter, the load lock chamber 4 is air-tightly closed and is evacuated by the vacuum device from the condition of atmospheric pressure to a vacuum condition. Then, the load lock chamber 4, the buffer chamber 3, and the etching chamber 6 are communicated with each other, and the sample

Though the chlorine-containing gas was used as the halogen-type gas for the etching treatment of the wiring film, the same effects are also obtained even when the bromine-type gas is used.

In the aforementioned treatment procedure, the methanol gas and the oxygen gas are mixed together to produce a plasma, in order to carry out the corrosion prevention treatment and the ashing treatment simultaneously. As shown in Figs. 5 and 6, however, it is also allowable to divide the step into those of the gas plasmas by changing the treatment gas, i.e., to divide the step into one of the corrosion prevention treatment and the one of the ashing treatment which are carried out after the etching treatment.

According to the procedure of treatment shown in Fig. 5, the resist component (C, H, etc.) is removed (ashing treatment) with the plasma of oxygen gas ( $O_2$ ) after the etching treatment. Then, the treatment gas is changed, and the residual matter (resist component, etc.) and the chlorine component are removed (corrosion prevention treatment) with the plasma of, in this case, the treatment gas of a mixture of oxygen gas ( $O_2$ ) and methanol gas ( $CH_3OH$ ). The treatment gas used for the corrosion prevention treatment may be a treatment gas consisting of a mixture of an inert gas such as helium or argon, a gas having  $N_2O$  or  $O_3$  and H components (such as methanol ( $CH_3OH$ ), ethanol ( $C_2H_5OH$ ), acetone ( $CH_3COCH_3$ ), hydrogen ( $H_2$ ), ethane ( $CH_4$ ) or the like), or a gas containing hydrogen component only, in addition to the treatment gas consisting of a mixture of oxygen gas ( $O_2$ ) and methanol gas ( $CH_3OH$ ). By using a gas having oxygen component, the effect for removing the residual matter can be expected.

According to the procedure of treatment shown in Fig. 6, the residual adhered matter and chlorine component adhered to the resist are removed with the plasma of a treatment gas of a mixture of an inert gas without containing oxygen component and a gas containing hydrogen component after the etching treatment and, then, the treatment gas is changed in order to remove the resist with the plasma of the oxygen gas ( $O_2$ ). Even in this case, the above-mentioned gases can be used as the treatment gases. Or, the treatment may be carried out while switching these gases.

According to this embodiment, as described above, the chlorine quantity remaining in the wiring film after the etching treatment can be greatly reduced compared with that of the prior art, and high corrosion prevention performance is imparted to the wiring film after the etching treatment.

The apparatus in the post-etch treatment portion in this embodiment is constituted by providing the porous plate 18 between the plasma generating chamber 17 and the post-etch treatment chamber 8

as shown in Fig. 2. It is, however, also allowable to directly treat the sample 16 with the plasma generated in the plasma generating chamber 17 without employing the porous plate. Further, the plasma is generated using microwaves. It is, however, also allowable to employ an RIE apparatus of the type of parallel flat plates using high-frequency electric power or any other system using high-frequency electric power such as a cylindrical-type apparatus, provided it is capable of generating plasma that contains hydrogen component and oxygen component.

In this embodiment, furthermore, the etching treatment and the post-etch treatment are incorporated in the same apparatus as shown in Fig. 1 and are continuously carried out. The invention, however, is in no way limited thereto only. That is, when the resist and the residual adhered matter are to be removed simultaneously, the subsequent additional treatment with the plasma of oxygen may be carried out in a separate treatment chamber which is provided on the outside of the apparatus that is shown in Fig. 1.

Furthermore, the resist may be removed by the widely known ashing treatment using the plasma of a mixture gas consisting of oxygen gas and a fluorine-type gas. The ashing treatment with the plasma of a mixture gas of oxygen gas and fluorine-type gas is effective for the corrosion prevention treatment particularly when a silicon-type material is contained in the resist material for forming pattern. When the silicon-type material (silicon-type inorganic resist or silicon photoresist) is used as the resist material, the ashing treatment with the oxygen radicals permit the silicon in the resist material to react with oxygen radicals to form silicon oxide that stays thereon, making it difficult to sufficiently carry out the ashing treatment for the resist. The remaining resist causes the wiring to corrode due to the residual chlorine or stays as foreign matter when an insulating film is to be formed on the wiring film causing poor insulation of the circuit, and deteriorates the yields of production. Therefore, the resist should be removed as much as possible.

The ashing treatment with the plasma of mixture gas of oxygen gas and fluorine-type gas is carried out after the plasma treatment (corrosion prevention treatment) that uses methanol or the mixture gas of methanol and oxygen, and that is effected after the etching treatment. Therefore, when the silicon-type material is used as the resist material component, the residual adhered matter and the resist that stay on the wiring film after the etching treatment can be effectively removed to accomplish high corrosion prevention performance. In the ashing treatment using the plasma of a mixture gas of oxygen and fluorine-type gas, fur-



is carried by a swing arm 5 into the etching chamber 6 evacuated into a vacuum condition via the buffer chamber 3 that is also evacuated into a vacuum condition. Thereafter, the etching chamber 6 is air-tightly closed to carry out a predetermined etching treatment therein. After the etching treatment is finished, the etching chamber 6, buffer chamber 3 and post-etch treatment chamber 8 are communicated with each other, and the sample is carried by a swing arm 7 into the post-etch treatment chamber 8 that is evacuated into a vacuum condition via the buffer chamber 3 that is evacuated into a vacuum condition. Thereafter, the post-etch treatment chamber 8 is air-tightly sealed to carry out a predetermined post-etch treatment therein. After the post-etch treatment is finished, the post-etch treatment chamber 8, the buffer chamber 3 and the load lock chamber 9 are communicated with each other, and the sample is carried by the swing arm 7 into the load lock chamber 9 that is evacuated into a vacuum condition via the buffer chamber 3 that has been evacuated to the vacuum condition. Then, the load lock chamber 9 is air-tightly closed, and a leakage gas such as  $N_2$  gas is introduced into the load lock chamber 9 to elevate the pressure up to the atmospheric pressure. Then, the load lock chamber 9 is opened, and the treated sample is delivered from the load lock chamber 9 by the go-straight arm 10 and is stored in the unload-side cassette 11 to complete a series of treatments.

Fig. 2 is a vertical section view of the sample treatment apparatus illustrating the portion of the post-etch treatment chamber 8 of Fig. 1. Over the post-etch treatment chamber 8 is provided a plasma generating chamber 17 that is partitioned by an aluminum porous plate 18. The upper opening of the plasma generating chamber 17 is closed by a window 19 of quartz, and a microwave waveguide 20 having a microwave oscillator 21 at the end is mounted on the opening. The plasma generating chamber 17 is provided with a gas feed port 22 to which is connected a gas feed pipe 23 to feed a treatment gas into the plasma generating chamber 17 from a gas feed source (not shown) via flow rate control valves 24 and 25. The post-etch treatment chamber 8 is provided with an exhaust port 12 to which is connected a vacuum device (not shown) via a pressure control valve 13 to evacuate the interior of the post-etch treatment chamber 8. The post-etch treatment chamber 8 is further provided with a sample plate 14 on which a sample 16 is placed being opposed to the plasma generating chamber 17. The sample plate 14 is equipped with a heating device 15 for heating the sample 16.

In the thus constituted sample treatment apparatus, the microwaves of a frequency of, in this case, 2.45 GHz generated by the microwave os-

cillator 21 are guided into the plasma generating chamber 17 propagating through the microwave waveguide 20 and the window 19. The microwaves introduced into the plasma generating chamber 17 excite the treatment gas that is introduced into the plasma generating chamber 17. Then, a plasma is generated in the plasma generating chamber 17. The aluminum porous plate 18 provided between the plasma generating chamber 17 and the post-etch treatment chamber 8 reflects the microwaves so as not to enter into the post-etch treatment chamber 8, and prevents the generation of plasma in the post-etch treatment chamber 8. The plasma and chiefly radical components in the plasma generating chamber 17 that has passed through the porous plate 18 is guided onto the sample 16 carried by the exhaust stream of the post-etch treatment chamber 8.

Using the continuous treatment apparatus shown in Figs. 1 and 2, the treatment is carried out according to the procedure shown in Fig. 3.

In the etching chamber 6, first, the sample 16 on which the wiring film (aluminum-containing wiring material) is formed is etched using a halogen-type gas. The etching treatment is carried out by using an RIE apparatus or a microwave apparatus. Described below is a case of the etching treatment carried out using, for example, a microwave etching apparatus in the presence of magnetic field wherein the sample to be treated is placed on the sample plate, a plasma of the treatment gas is formed by the action of electric field of the microwaves and magnetic field of the solenoid coil, and the sample is etched by the application of a high-frequency bias. In this case, the sample 16 on which the wiring film is formed is obtained by forming a heat oxidized film ( $SiO_2$ ) maintaining a thickness of 600nm on the silicon substrate, and then forming a TiN film, an Al-Si (1%) - Cu (0.5%) film, and TiN film thereon maintaining thicknesses of 100nm, 700nm and 50nm, respectively, and then forming a resist film thereon maintaining a thickness of 1800nm. Further, the wiring pattern is formed in the resist film which is used as a mask for etching. Further, a mixture gas consisting of  $BCl_3$  (60cc/min.) and  $Cl_2$  (90cc/min.) is used as the halogen-type gas. The etching treatment is carried out under the conditions of a pressure of 2.1 Pa, microwave current of 300mA, and high-frequency electric power of 90 watts.

After the etching treatment of the sample 16, there remain components that cause the sample 16 to corrode due to the reasons mentioned in the foregoing prior art. That is, the resist which is a masking material remains on the wiring pattern that is formed by etching, and halogen which, in this case, is chlorine component remains in the resist and on the surface of the resist. Further, the resid-

ual adhered matter consisting of aluminum, chlorine, carbon, hydrogen, etc. remains on the side walls of the wiring pattern.

Next, the sample 16 on which the resist and residual adhered matter remain is sent to the post-etch treatment chamber 8 to effect the post-etch treatment which is carried out as described below. That is, the flow rates of an oxygen gas ( $O_2$ ) and a methanol gas ( $CH_3OH$ ) containing hydrogen component are adjusted by the flow rate control valves 24 and 25, and these gases are mixed together and are introduced into the plasma generating chamber 17. In this case, for instance, the flow rate of oxygen gas is 400cc/min., the flow rate of methanol gas is 80cc/min., and the pressure in the post-etch treatment chamber 8 is 160 Pa. Next, the microwaves are introduced into the plasma generating chamber 17 from the microwave oscillator 21. For instance, the microwave output in this case is 400mA. Then, a plasma of hydrogen component (H), oxygen component (O) and other components is generated in the plasma generating chamber 17. In this case, the plasma consisting chiefly of radicals is guided into the post-etch treatment chamber 8 accompanying the evacuating exhaust stream. Radicals are chiefly comprised of hydrogen and oxygen. The hydrogen radicals react with the chlorine component (Cl) in the residual adhered matter (Al, Cl, C, H, etc.) to form hydrogen chloride (HCl) which volatilizes or forms  $H_2O$  to dissolve the elute chlorine component contributing presumably to removing residual chlorine component that is a cause of corrosion to the wiring film. Further, the oxygen radicals react with the resist to form CO and  $CO_2$  that volatilize, so that the organic components composed chiefly of resist are removed.

Thus, the wiring film after the etching treatment is treated using the plasma of the treatment gas consisting of a mixture of methanol gas and oxygen gas, and whereby the resist and the residual adhered matter remaining on the sample are removed and, further, the chlorine components remaining on the surface and inside the sample which cause corrosion are removed. This makes it possible to obtain corrosion prevention performance of longer than 24 hours even in a clean room environment. Since the treatment is carried out while removing the resist, the ashing treatment can be effected at the same time. At this moment, the sample plate 14 is heated by the heating device 15 to heat the sample that is being treated with plasma. Therefore, the chemical reaction of the residual adhered matter or the resist with the radicals is assisted to more efficiently remove the residual matter (residual adhered matter and resist) after the etching treatment.

As concrete examples of treatment, described below in conjunction with Fig. 4 are the conven-

tional post-etch treatment and the post-etch treatment of this embodiment in comparison with each other using an aluminum film as the wiring film.

Fig. 4 is a diagram showing the residual chlorine quantity reducing effect according to this embodiment. The treatment A of Fig. 3 shows the residual chlorine quantity of the case when the treatment is effected for two minutes in a customary manner using the plasma of a mixture gas consisting of oxygen ( $O_2$ ) and carbon tetrafluoride ( $CF_4$ ). The treatment B shows the residual chlorine quantity of the case when the treatment is effected for one minute using a mixture gas consisting of methanol ( $CH_3OH$ ) and oxygen ( $O_2$ ). In the treatment B, the additional treatment is effected for one minute using the plasma of oxygen to prevent the resist from remaining after the treatment using the mixture gas. The sample is an aluminum-film wafer with a 6-inch wiring pattern, the aluminum film having a thickness of 800nm.

The treatment A is carried out under the conditions of an oxygen flow rate of 400cc/min, a carbon tetrafluoride flow rate of 20cc/min and a treatment pressure of 160 Pa. The treatment B is first carried out under the conditions of a methanol flow rate of 80cc/min, an oxygen flow rate of 400cc/min and a treatment pressure of 160 Pa., and is then carried out under the conditions of an oxygen flow rate of 400cc/min and a treatment pressure of 160 Pa. The treatment B is carried out while setting the sample plate temperature at  $250^\circ C$  such that the resist ashing rate becomes nearly equal to the values of when a mixture gas of oxygen and carbon tetrafluoride is used. The sample plate 14 should be set at a temperature of  $200^\circ C$  to  $350^\circ C$  from the relationship of the ashing rate of the resist and the thermal damage to the aluminum film.

As shown in Fig. 4, the treatment with the plasma of a gas containing hydrogen and oxygen according to this embodiment makes it possible to decrease the residual chlorine content to less than about one-half compared with that of the prior art. Therefore, the corrosion prevention performance of longer than 24 hours is obtained even under clean room environment.

As described above, it is better to reliably remove the resist by effecting the additional treatment with the plasma of an oxygen gas after the treatment with the plasma of a gas containing hydrogen component and oxygen component such as methanol or with the plasma of a mixture gas of methanol or the like and oxygen. When the residual adhered matter and resist can be removed by the treatment with the plasma of a mixture gas of methanol or the like and oxygen, however, the additional treatment with the plasma of oxygen shown in Fig. 3 needs not be carried out.



thermore, the sample plate should be maintained at a temperature of lower than 50° C when the sample 17 is composed of a barrier metal in order to prevent side etching of TiN film or TiW film that lies under the wiring film.

A second embodiment of the present invention will now be described in conjunction with Fig. 7.

In Fig. 7, the same reference numerals as those of Fig. 2 denote the same members and their description is not repeated here. What makes Fig. 7 different from Fig. 2 is that the post-etch treatment chamber 8 is provided with a feed port 26 to which is connected a feed pipe 27 that is connected, via a flow rate control valve 28, to a gas feed source (not shown) for adsorption/desorption treatment, so that a gas for adsorption/desorption treatment can be supplied into the post-etch treatment chamber 8.

With the thus constituted apparatus, the sample 16 after the etching treatment with the plasma of a halogen-type gas is subjected to the treatment for removing resist in the post-etch treatment chamber 8 using the plasma of an oxygen gas which is one of the methods mentioned in the foregoing first embodiment. Thereafter, the residual components that cause corrosion are removed as described below.

First, the gas for adsorption/desorption treatment is supplied at a controlled flow rate into the post-etch treatment chamber 8 from the source (not shown) of feeding the gas for adsorption/desorption treatment via the flow rate control valve 28 and the feed pipe 27. The gas, in this case, is that of pure water component or, concretely, vaporized gas of pure water. At this moment, the pressure control valve 13 for controlling the pressure in the post-etch treatment chamber 8 is maintained closed. This causes the pressure in the post-etch treatment chamber 8 to rise. Next, when a preset pressure in the post-etch treatment chamber is exceeded, i.e., when a pressure region denoted by A in Fig. 8 (pressure higher than the one that condenses the introduced gas) is reached that is above a saturated vapor pressure curve, supply of the gas is discontinued, and the pressure control valve 13 is opened. For instance, the sample plate temperature in this case is about 20° C, and the operation is repeated twice in which the pressure in the post-etch treatment chamber 8 is raised from 67 Pa to 4000 Pa and is decreased again down to 67 Pa each time.

By repeating the above-mentioned operation, the component that causes corrosion or halogen component, in this case, is dissolved and diluted on the sample surface after the ashing treatment owing to the adsorption of the introduced vaporized gas of pure water and the dropping of liquid formed by the rise in gas pressure. Thereafter, the

interior in the post-etch treatment chamber 8 is evacuated (the pressure in the post-etch treatment chamber 8 is decreased into a region denoted by B in Fig. 8) to promote the vaporization and desorption of pure water in which are dissolved halogen components adhered onto the sample surface. This makes it possible to greatly decrease the amount of halogen components adhered on the sample, and the corrosion protection performance of longer than 24 hours is obtained even under a clean room environment.

According to the second embodiment which greatly decreases the amount of halogen remaining after the etching treatment and ashing treatment of the wiring film, it is allowed to obtain improved corrosion prevention performance. Moreover, no water-washing apparatus is needed. In addition, resist removing means is incorporated. Therefore, the treatment is carried out consistently in series from the etching treatment through the resist removal treatment up to the corrosion prevention treatment, making it possible to shorten the time for carrying samples among the treatment apparatuses and to shorten the waiting time, contributing to improving production efficiency. Moreover, since no water-washing apparatus is needed, the apparatus can be realized in a compact size.

Next, a third embodiment will be described in conjunction with Fig. 9. The apparatus used in this embodiment consists of the apparatus shown in Fig. 2 but which is further equipped with temperature adjusting means (consisting of a constant temperature water vessel 30 and a cooling water flow path 29) for controlling the temperature of the sample plate 14.

According to this embodiment like the aforementioned second embodiment, the sample 16 is subjected to the etching treatment and the resist removal treatment, and the vaporized gas of pure water is introduced into the post-etch treatment chamber 8 in order to effect the adsorption and desorption of components that remain and cause corrosion to the sample 16. At this moment, the sample plate 14 on which the sample 16 is placed is maintained at a temperature of 0° C to 20° C which is lower than room temperature owing to the temperature adjusting means. In the adsorption/desorption treatment of the sample 16, therefore, the sample plate 14 and the sample 16 have a temperature lower than the periphery thereof, e.g., lower than the side walls of the post-etch treatment chamber 8 at the time of adsorption and desorption of the introduced gas, and the introduced gas is adsorbed in a concentrated manner. Therefore, the components, i.e., halogen components that are remaining on the sample 16 and that are causes of corrosion, are dissolved and diluted efficiently, enabling the halogen quantity remaining

after the desorption to be greatly decreased.

This embodiment makes it possible to further enhance the corrosion prevention performance than the aforementioned embodiments.

According to this embodiment, the resist is removed after the etching treatment and, then, the adsorption and desorption are carried out to decrease the halogen component that remains on the sample to corrode it. However, it is also allowable to add the desorption promotion treatment (in this embodiment, the sample is heated while treating it with the plasma of oxygen after the adsorption and desorption) to carry out the treatment in series). This makes it possible to vaporize and remove the water content containing halogen component remaining after the adsorption and desorption and, hence, to obtain higher corrosion preventing performance than that of the second embodiment.

A fourth embodiment will now be described in conjunction with Fig. 10.

In Fig. 10, the load lock chamber 9 shown in Fig. 1 is equipped with heating means to heat the sample 16 that is to be treated, and feeding means is provided to feed a gas for adsorption/desorption treatment into the load lock chamber 9. The heating means consists of a heating device 34 placed on a quartz glass 33 that hermetically closes the upper opening of the load lock chamber 9. The heating device 34 in this case is a lamp heater. The feeding means for feeding a gas for adsorption/desorption treatment consists as in the second embodiment of providing the load lock chamber 9 with a feed port 35 to which is connected, via a flow rate control valve 37, a feed pipe 36 that is connected to the source (not shown) that feeds the gas for adsorption/desorption treatment. Reference numeral 38 denotes an exhaust port formed in the load lock chamber 9. An exhaust device (not shown) is connected to the exhaust port 38 via an exhaust pipe 39 and a pressure control valve 40. Reference numeral 41 denotes an exhaust port formed in the buffer chamber 3. An exhaust device (not shown) is connected to the exhaust port 41 via a pressure control valve 42. The sample plate 31 moves up and down, and comes in contact with the upper opening in the buffer chamber 3 to form the load lock chamber 9. The device for pushing up the sample 16 works to easily hand the sample 16 over to the carrier device such as the swing arm at the time of delivering the sample into or out of the buffer chamber 3 or the load lock chamber 9. The load lock chamber 9 is the one which communicates the vacuum chamber with the open atmosphere. In order to evacuate into vacuum condition or to return the pressure to the atmospheric pressure, the load lock chamber 9 has space which is as small as possible such that the pressure condition can be

quickly changed.

With the thus constituted apparatus, the etching treatment and the resist removal treatment are carried out in the same manner as in the aforementioned first embodiment. That is, the etching treatment is effected with the plasma of the halogen-type gas in the etching chamber and, then, the resist is removed in the post-etch treatment chamber using the plasma of, for example, an oxygen gas which is one of the methods mentioned in the foregoing first embodiment. After the resist removal treatment, the sample 16 is introduced into the load lock chamber 9 shown in Fig. 10, and the halogen components that are causes of corrosion are removed as described below.

First, like in the treatment in the aforementioned second embodiment, the gas for adsorption/desorption treatment such as vaporized gas of pure water is supplied at a controlled flow rate into the load lock chamber 9 from the source (not shown) of feeding gas for adsorption/desorption treatment via the flow rate control valve 37 and the feed pipe 36. At this moment, the pressure control valve 40 for controlling the pressure in the load lock chamber 9 is maintained closed. This causes the pressure in the load lock chamber 9 to rise. Next, when the present pressure is reached in the load lock chamber, i.e., when a pressure region indicated by A in Fig. 8 (pressure higher than the one capable of condensing the introduced gas) is reached that is above the saturated vapor pressure curve, the supply of gas is discontinued, the pressure control valve 40 is opened, and the interior of the load lock chamber 9 is evacuated (the pressure in the load lock chamber 9 is reduced to be shifted to the region indicated by B in Fig. 9). For instance, the operation is repeated twice in which the sample plate temperature is maintained at about 20°C, the pressure in the post-etch treatment chamber 8 is raised from 67 Pa to 4000 Pa and is decreased again to 67 Pa each time, in the same manner as in the processing of the aforementioned second embodiment. Next, the sample 16 is heated by the heating device 34 (lamp heater).

By effecting the above-mentioned operation, the halogen components that are causes of corrosion are dissolved and eluted on the surface of the sample after the resist removal treatment owing to the adsorption of the introduced gas and the liquefaction by the rise in the gas pressure. Thereafter, the interior of the load lock chamber 9 is evacuated to promote the vaporization and desorption of pure water in which are dissolved and diluted halogen components remaining on the sample surface. This makes it possible to greatly decrease the amount of halogen components adhered to and remaining on the sample. By heating the

plasma  
+  
H<sub>2</sub>O  
?  
or  
H<sub>2</sub>O + D  
only  
no  
plasma  
?



3. A method according to claim 2, wherein the gas having the oxygen component is oxygen ( $O_2$ ) gas or a mixture consisting of oxygen ( $O_2$ ) and a fluorine-type gas.

4. A method according to any one of claims 1 to 3, wherein said corrosion prevention treatment is carried out using the plasma of the gas that has the hydrogen component.

5. A method according to claim 4, wherein the gas having the hydrogen component is any one of methanol ( $CH_3OH$ ), ethanol ( $C_2H_5OH$ ), acetone ( $CH_3COCH_3$ ), hydrogen ( $H_2$ ) and methane ( $CH_4$ ), or a mixture consisting of at least one of these gases and any one of an inert gas,  $N_2O$ ,  $O_2$  and  $O_3$ .

6. A method according to any one of claims 1 to 3, wherein the corrosion prevention treatment is carried out by liquefying the gas having the hydrogen component into droplets thereof on the sample and permitting the droplets to be vaporized again.

7. A method according to claim 6, wherein the gas having the hydrogen component is a vaporized gas of pure water ( $H_2O$ ).

8. A method of etching a sample of aluminum-containing material using a halogen gas and treating the sample after the etching by a step of effecting treatment using a plasma which has at least a hydrogen component, and a step of effecting treatment using a plasma which has an oxygen component.

9. A method according to claim 8, wherein the resist is removed in a first step using the plasma that has the oxygen component, and the corrosion prevention treatment is effected in a second step using the plasma that has the hydrogen component.

10. A method according to claim 8, wherein the corrosion prevention treatment is effected in a first step using the plasma that has the hydrogen component, and the resist is removed in a second step using the plasma that has the oxygen component.

11. A method according to any one of claims 8, 9 and 10, wherein the plasma having the hydrogen component is a plasma of a gas of any one of methanol ( $CH_3OH$ ), ethanol ( $C_2H_5OH$ ), acetone ( $CH_3COCH_3$ ), hydrogen ( $H_2$ ) and methane ( $CH_4$ ), or is the plasma of a gas of a mixture of at least one of these gases and any one of an inert gas,  $N_2O$ ,  $O_2$  and  $O_3$ .

12. A method according to any one of claims 8 to 11 wherein the plasma having the oxygen component is a plasma of oxygen ( $O_2$ ) gas or of a mixture gas of oxygen ( $O_2$ ) and a fluorine-type gas.

13. A method of etching a sample of aluminum-containing material using a halogen gas and treating the samples after the etching by effecting a corrosion prevention treatment using a plasma that has at least a hydrogen component and an oxygen

component.

14. A method according to claim 13, wherein the plasma having the hydrogen component and oxygen component is a plasma of a mixture of (i) any one of methanol ( $CH_3OH$ ), ethanol ( $C_2H_5OH$ ), acetone ( $CH_3COCH_3$ ), hydrogen ( $H_2$ ) and methane ( $CH_4$ ), and (ii) any one of oxygen ( $O_2$ ),  $O_3$  and  $N_2O$ .

15. A method according to claim 13 or claim 14 including a further step of effecting a treatment using a plasma of a mixture of oxygen and a fluorine-type gas after the said corrosion prevention treatment.

16. A method according to any one of claims 2,4,8 and 13 wherein said plasma is generated using microwaves.

17. A method according to claim 16, wherein said plasma is generated using microwaves of a power of 200W to 4KW under a treatment pressure of 0.4 to 2 Torr.

18. A method according to claim 8 or claim 13, wherein said aluminum-containing wiring material is treated at a temperature of 100°C to 300°C.

sample 16 by the heating device 34, furthermore, the water content remaining after the adsorption/desorption operation is removed by evaporation. Therefore, the effect by the halogen component-containing water decreases, and high corrosion protection performance is obtained.

This embodiment makes it possible to obtain high corrosion prevention performance as described above. Furthermore, since the load lock chamber 9 having small inner space is used as the treatment chamber, the vaporized gas of pure water needs be supplied in small amounts compared with the desorption treatment of residual halogen components by dissolution and delution in the post-etch treatment chamber 8. Furthermore, a good response in the pressure change enables the throughput to be improved. Further, since the sample 16 is directly heated by the heating device 34, the time of desorption treatment can be shortened compared with the time of desorption treatment by the heating with oxygen plasma in the post-etch treatment chamber 8 mentioned in the foregoing third embodiment. This makes it possible to increase the amount of treating the samples per a unit time in carrying out the treatment continuously and consistently.

In this embodiment, the halogen components are dissolved and diluted using the vaporized gas of pure water in the load lock chamber 9, and the pure water in which the halogen components are dissolved and diluted is subjected to the vaporization/desorption treatment, and the water remaining after the adsorption/desorption operation by the heating device 34 is removed by vaporization. It is, however, also allowable to dissolve and dilute the halogen components using the vaporized gas of pure water in the post-etch treatment chamber 8 followed by the evaporation/desorption treatment of pure water in which the halogen components are dissolved and diluted, and to remove by vaporization the water that remains after the adsorption/desorption operation using the heating device 34 in the load lock chamber 9. In this case, the load lock chamber 9 should be provided with the heating device 34 only.

According to the present invention as described above, the components that are causes of corrosion after the etching treatment of the wiring film are effectively decreased, and high corrosion prevention performance is imparted to the wiring film.

Moreover, the apparatus is constituted in a compact size contributing to improving the productivity.

Further, the features of the apparatus of the present invention are as follows:

1. A sample treatment apparatus for treating aluminum-containing wiring materials, compris-

ing an etching chamber, a post-etch treatment chamber, means for introducing a sample into the etching chamber, means for carrying the sample from said etching chamber into said post-etch treatment chamber, means for delivering the sample from said post-etch treatment chamber, means for feeding a gas for adsorption/desorption into said post-etch treatment chamber, and an exhaust device for evacuating the interior of said post-etch treatment chamber.

2. A sample treatment apparatus for treating aluminum-containing materials comprising means for etching the sample, means for removing resist from the sample after the etching, means for evacuating the chamber in which the sample is placed after the resist has been removed, means for starting and stopping the evacuation of said chamber, and means for feeding a gas for adsorption/desorption into the chamber in which said sample is placed.

3. A sample treatment apparatus as set forth in 2 above, wherein the chamber in which the sample is placed is the one in which the resist is removed.

4. A sample treatment apparatus as set forth in 2 above, wherein the chamber in which the sample is placed is the one which is different from the chamber in which the resist is removed but is the one of before the sample is being delivered into the open air.

5. A sample treatment apparatus as set forth in 4 above, wherein the chamber of before the sample is delivered into the open air is the load lock chamber.

6. A sample treatment apparatus as set forth in 2 above, wherein said chamber is provided with means for heating said sample.

7. A sample treatment apparatus as set forth in 2 above, wherein said chamber is provided with means for cooling said sample.

8. A sample treatment apparatus as set forth in 4 above, wherein said chamber is provided with means for heating said sample.

## Claims

1. A method of etching a sample of aluminum-containing material using a halogen gas and treating the sample after the etching by a step of removing the resist using a gas having an oxygen component; and a step of effecting a corrosion prevention treatment using a gas having the hydrogen component.
2. A method according to claim 1, wherein said resist is removed using a plasma of the gas that has the oxygen component.

FIG. 1

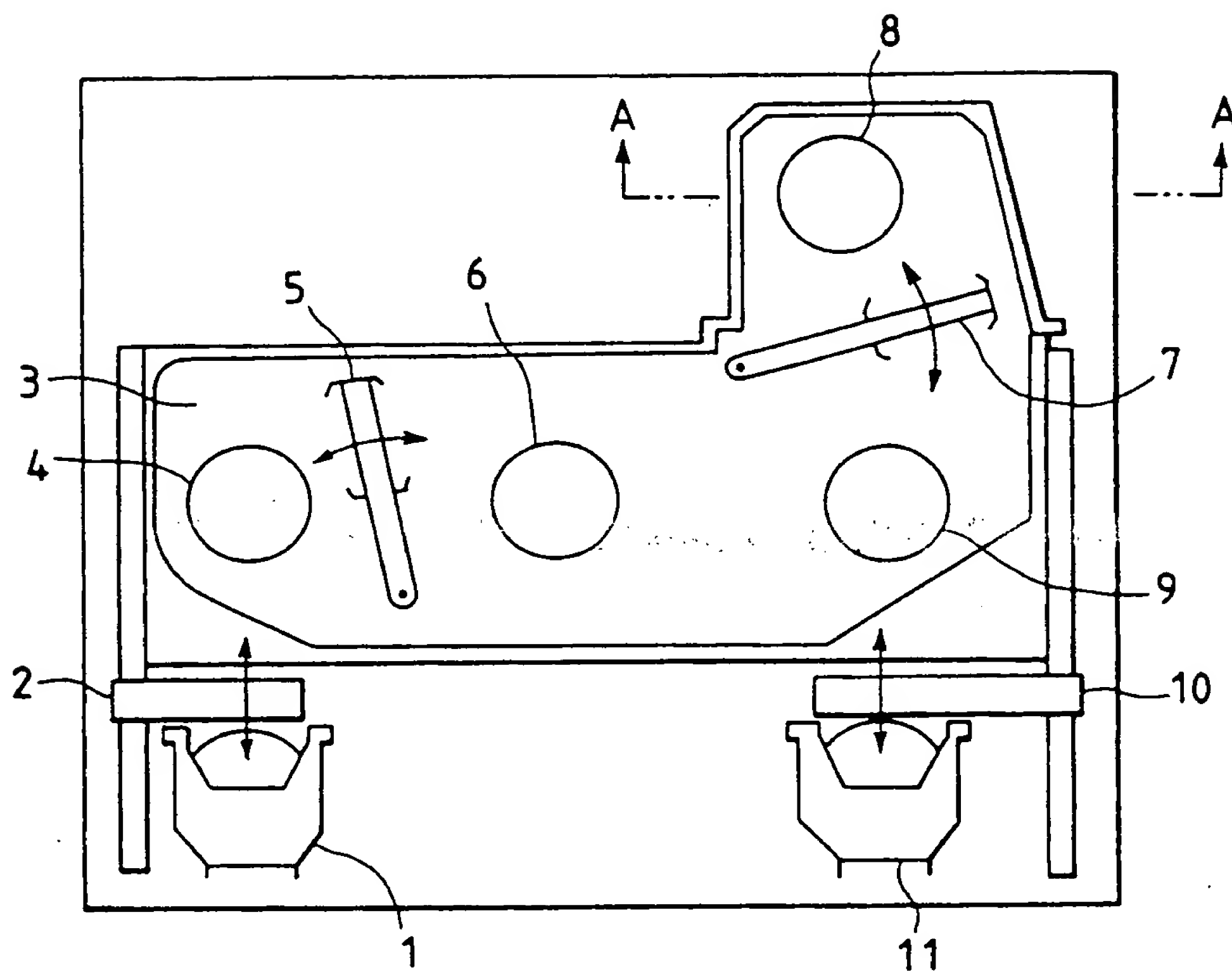


FIG. 2

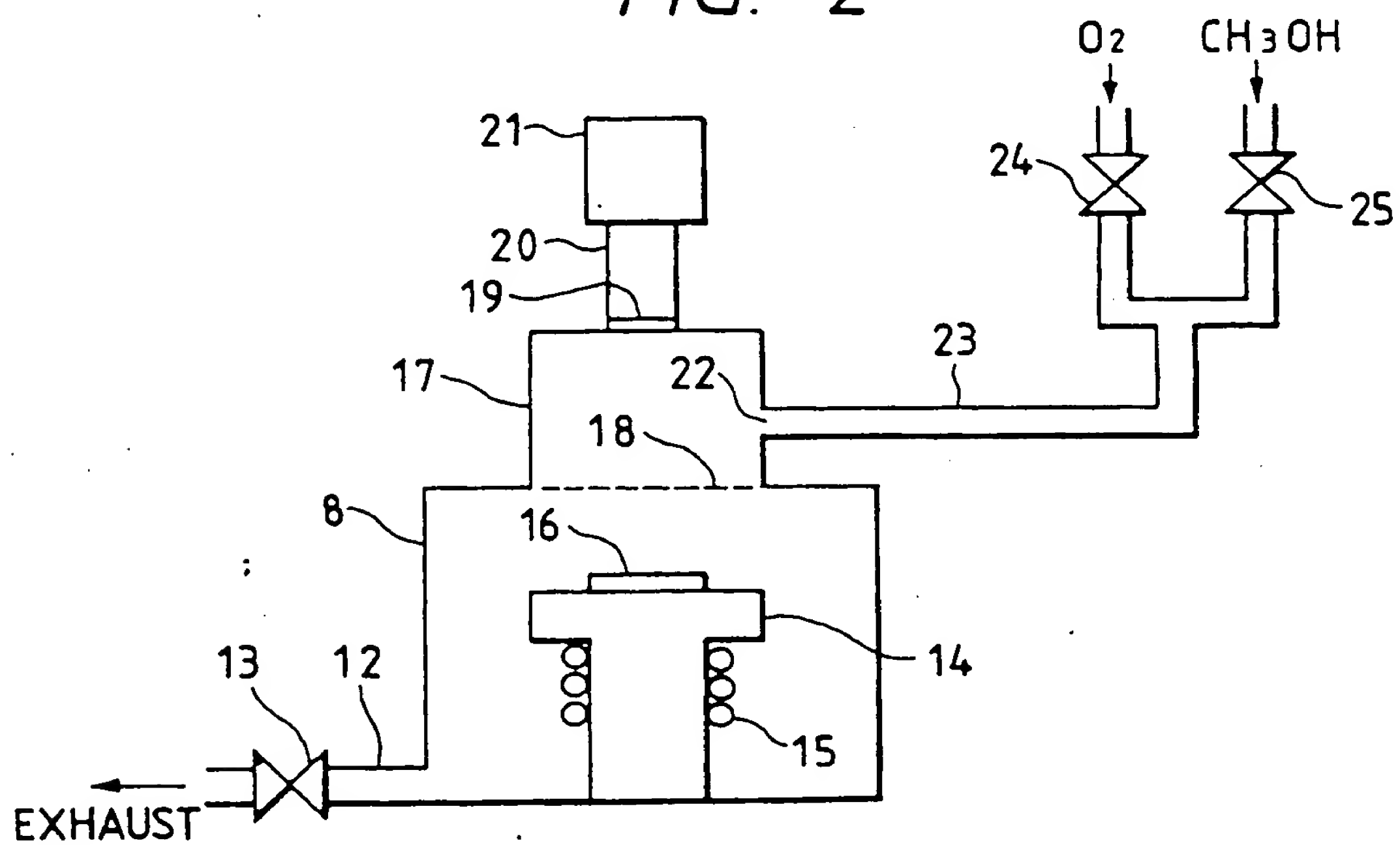




FIG. 3

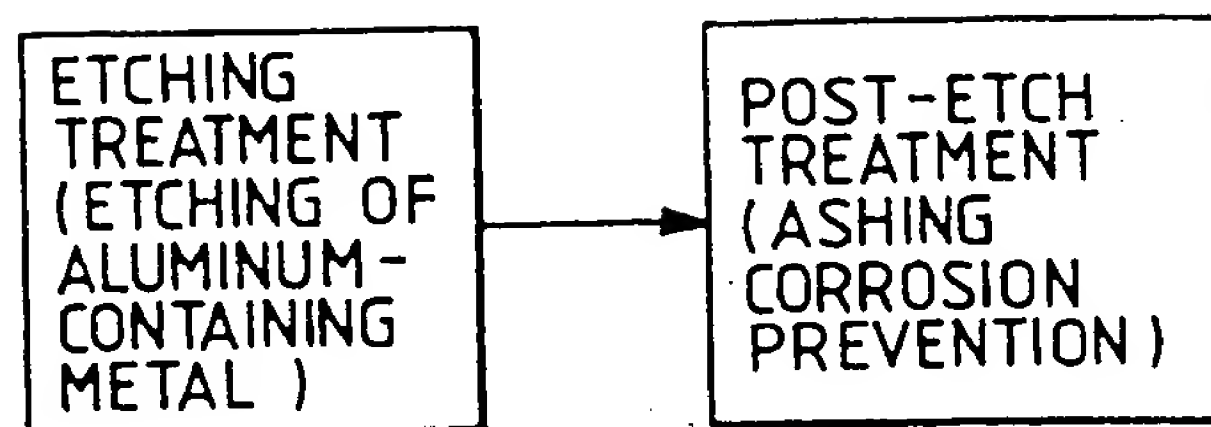


FIG. 4

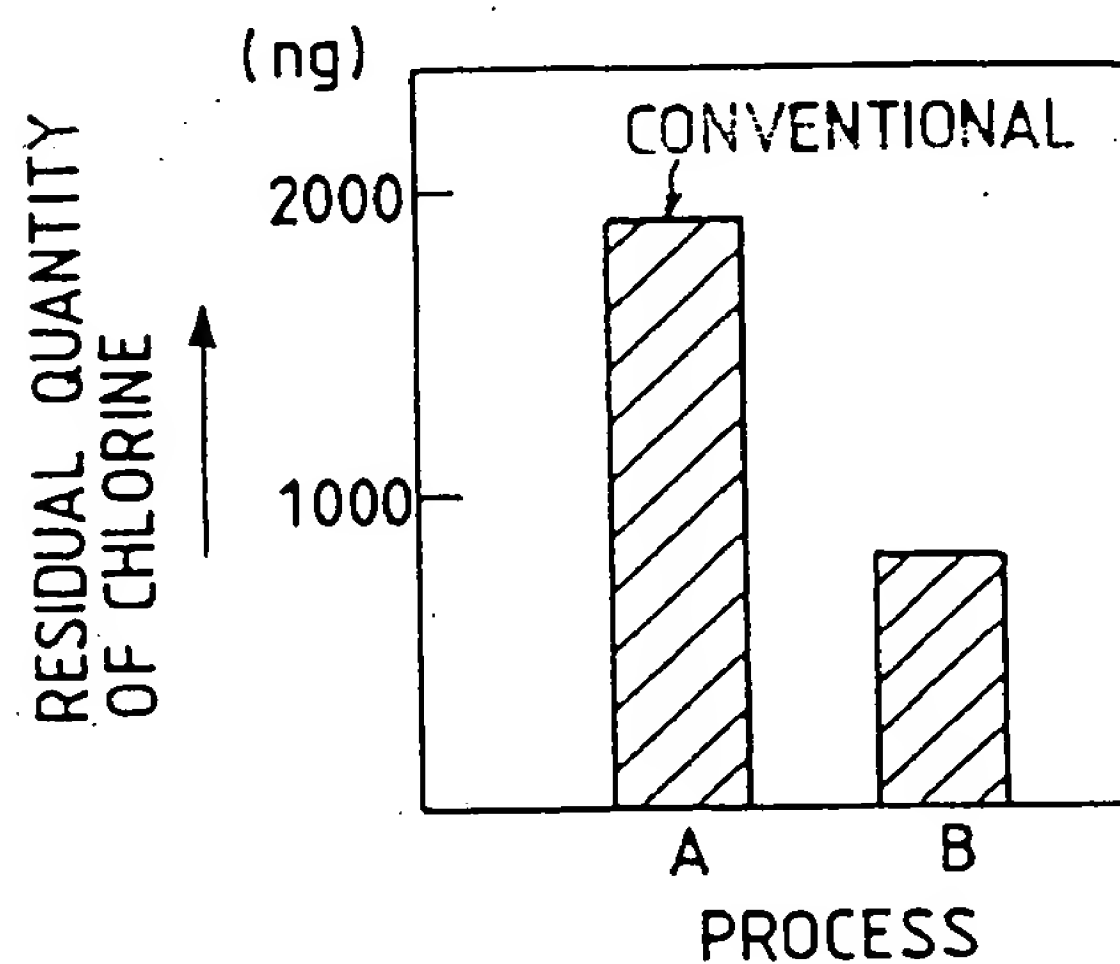


FIG. 5

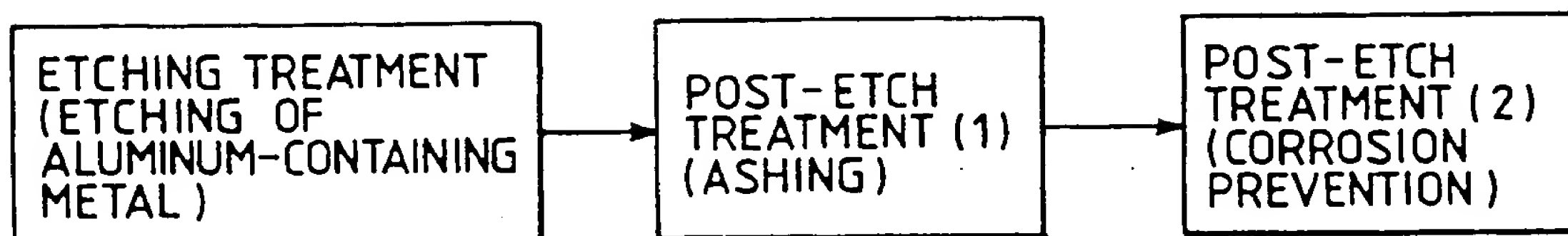


FIG. 6

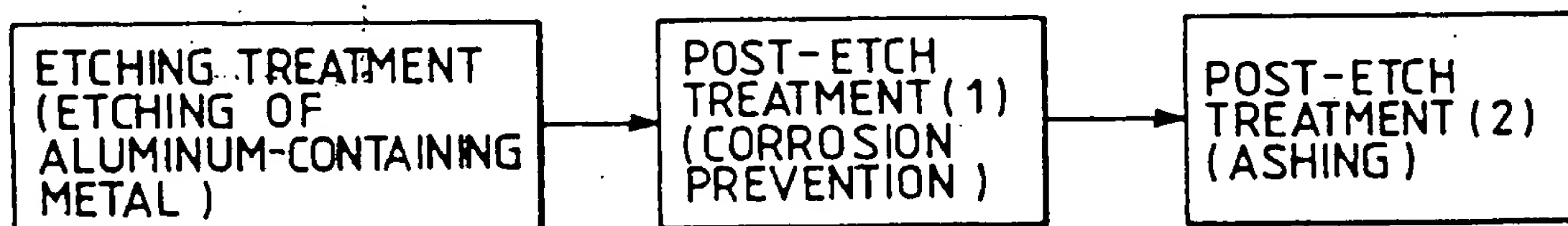


FIG. 7

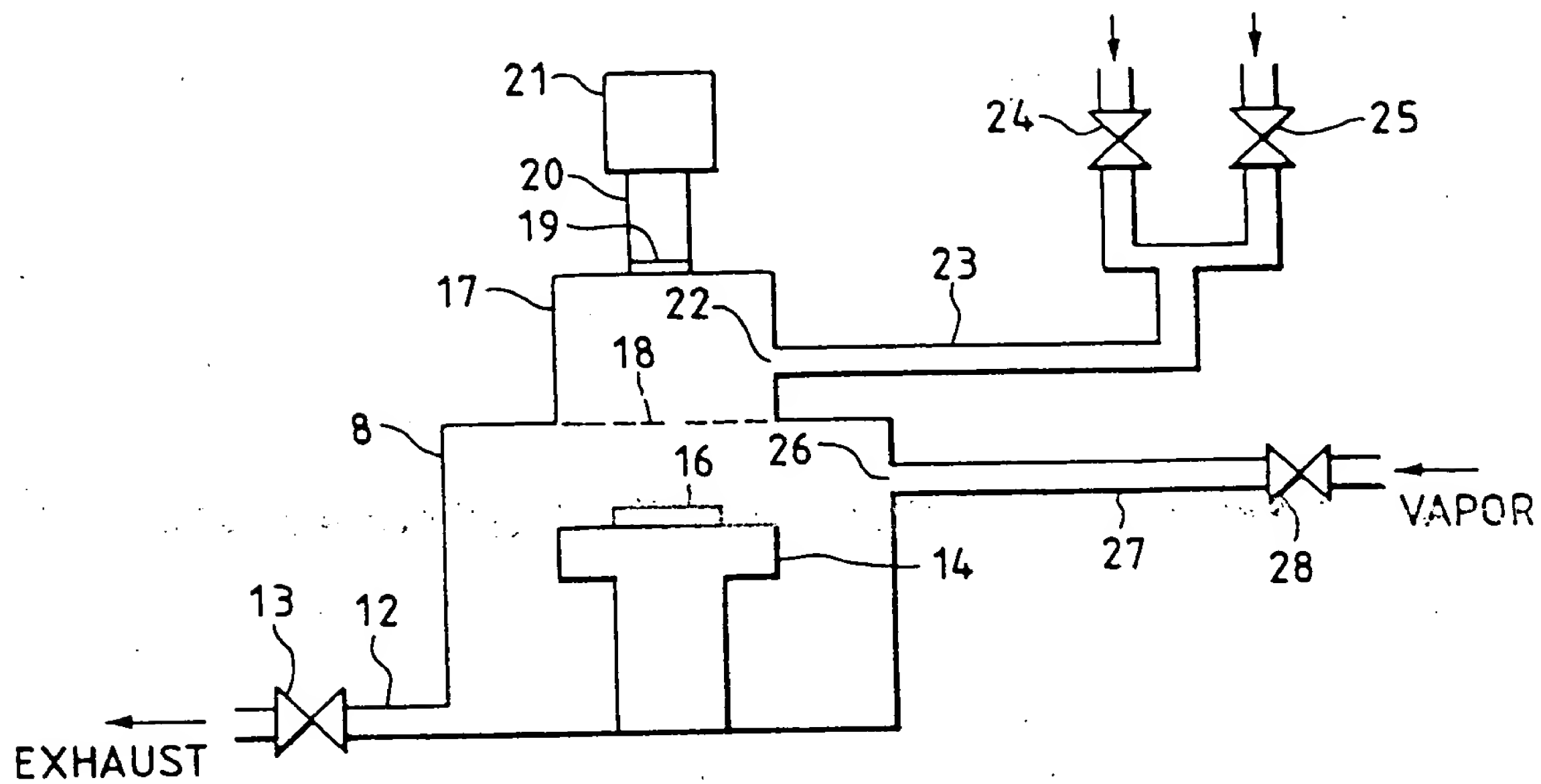


FIG. 8

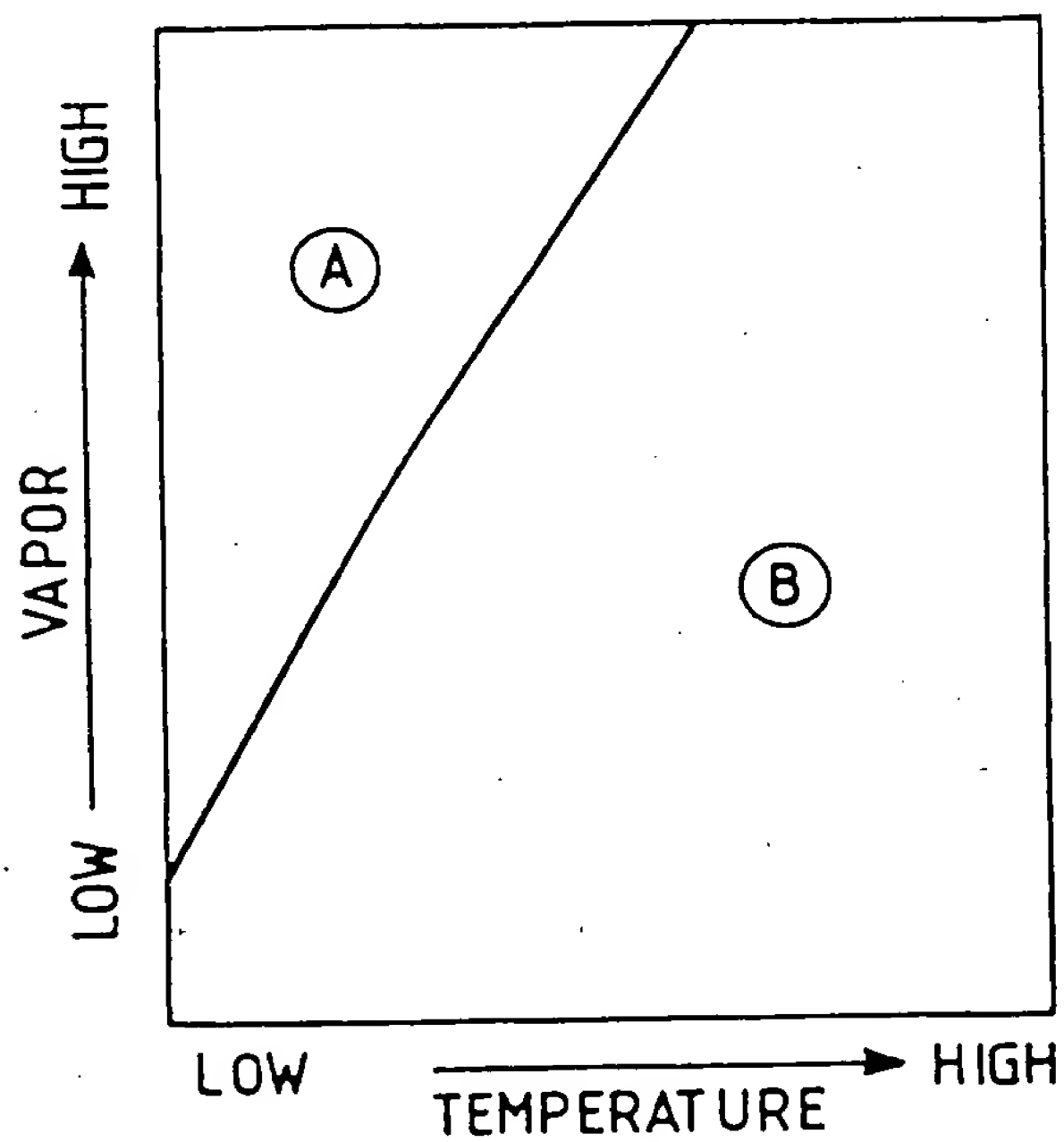


FIG. 9

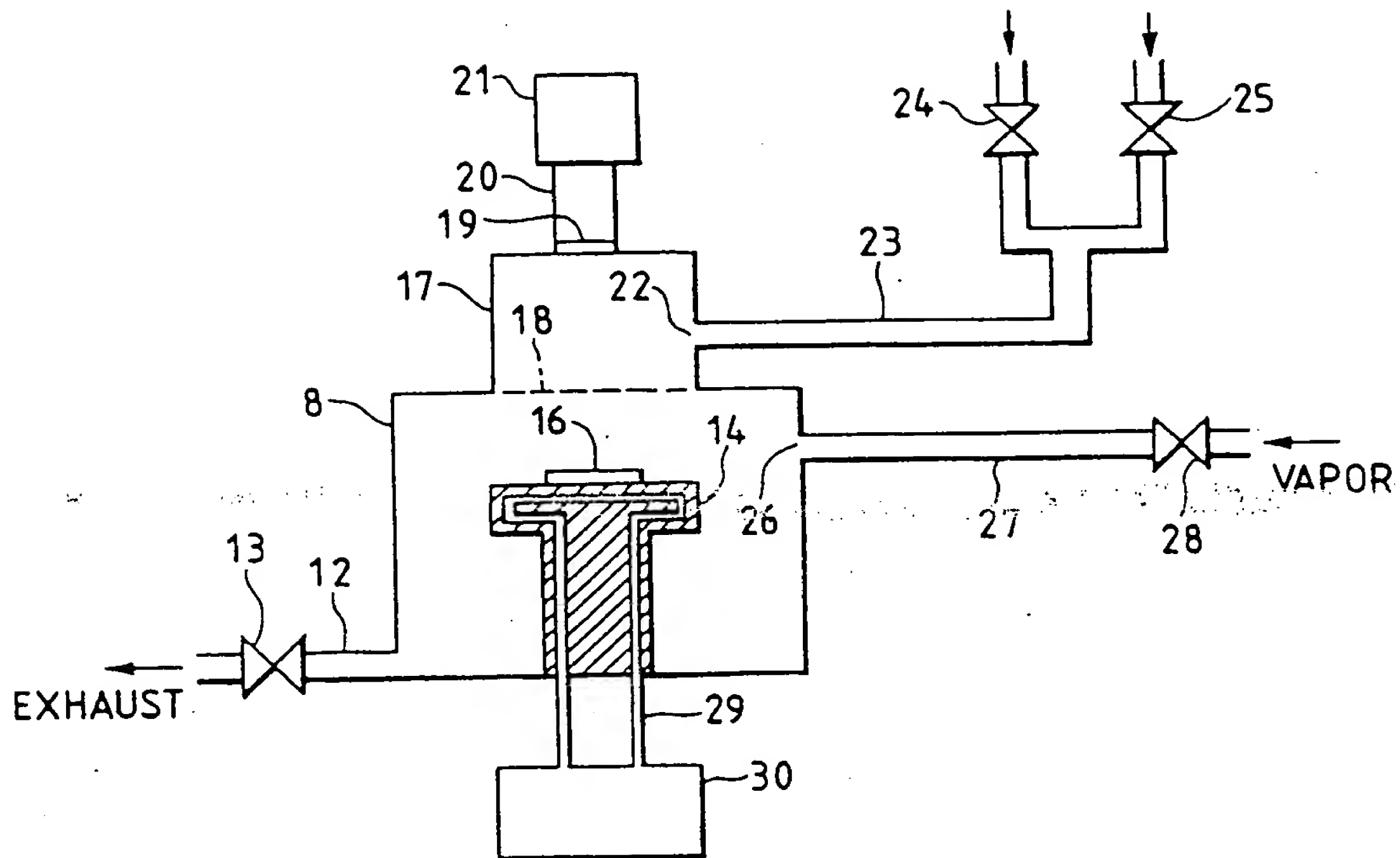
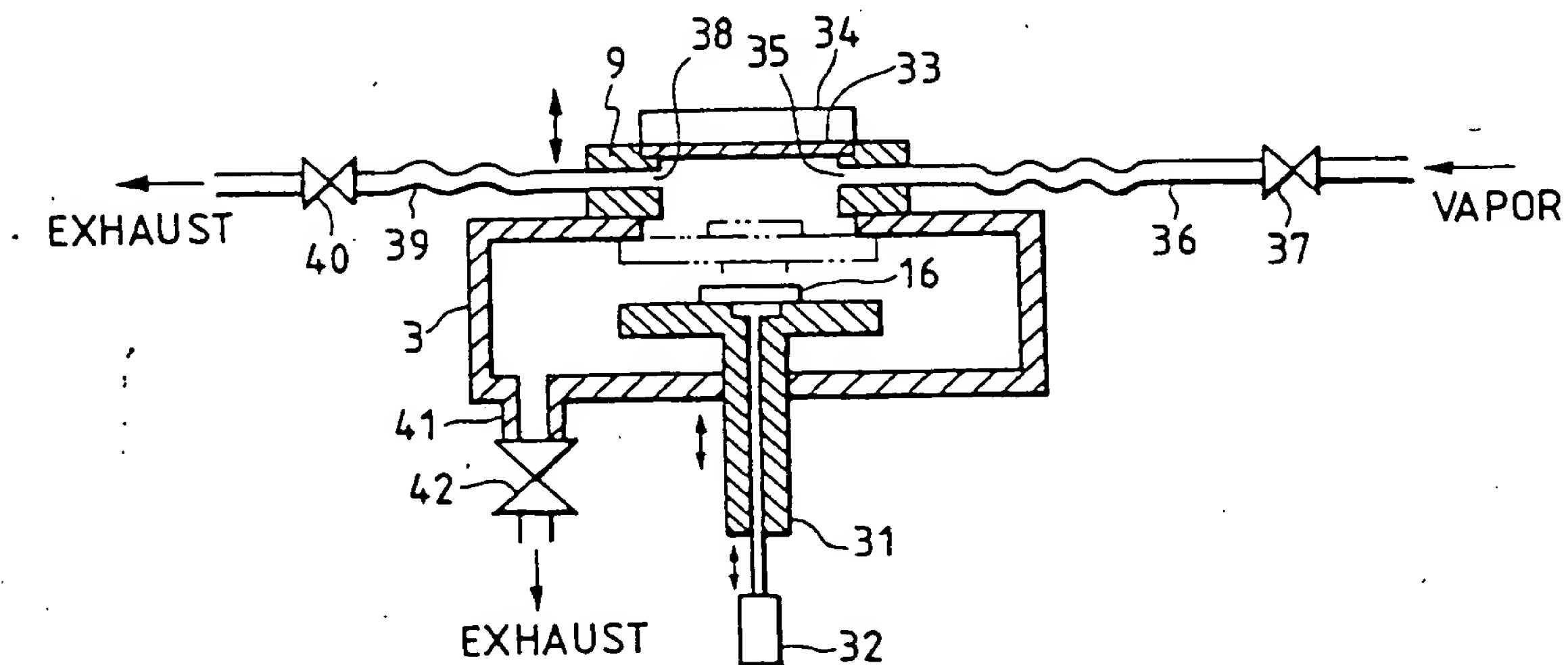


FIG. 10







European  
Patent Office

# EUROPEAN SEARCH REPORT

Application Number

EP 90 30 9106

## DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	EP-A-0 078 224 (FAIRCHILD CAMERA & INSTRUMENT) * Page 3, line 7 - page 4, line 20 *	8,13	H 01 L 21/321
A	---	1-4	
X	EP-A-0 140 201 (ASAHI GLASS) * Page 4, line 8 - page 11, line 18 *	13	
X	EP-A-0 247 603 (FUJITSU) * Page 3, line 47 - page 4, line 14; page 5, lines 7-10 *	13,18	
A	---	1-3,8-10, 12,15-17	
A	EXTENDED ABSTRACTS, vol. 80-2, October 1980, pages 851-853, abstract no. 329, Princeton, NJ, US; J.R. KITCHER: "Application of plasma etching to multilevel metal structures" * Page 852, last paragraph *	1,6,7	
A	IBM TECHNICAL DISCLOSURE BULLETIN, vol. 22, no. 8A, January 1980, page 3196, New York, US; C. CRIMI et al.: "Etching of aluminum and aluminum-copper alloys" * Whole document *	5,7,11,14	
A	EXTENDED ABSTRACTS, vol. 81-2, October 1981, pages 707-709, abstract no. 290, Pennington, NJ, US; D.K. RANADIVE et al.: "Multicycle process for aluminum plasma etching" * Page 707, paragraph 3 *	1-5,8-15	H 01 L
A	PROCEEDINGS OF THE ELECTROCHEMICAL SOCIETY, vol. 83, 1983, pages 341-352, Electrochem. Soc. Pub., Pennington, NJ, US; T. TSUKADA et al.: "After corrosion treatment in aluminum alloy reactive ion etching" * Abstract; figure 2 *		
The present search report has been drawn up for all claims			
Place of search		Date of completion of search	Examiner
The Hague		14 November 90	GORI P.
CATEGORY OF CITED DOCUMENTS		E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons ----- &: member of the same patent family, corresponding document	
X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention			